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Towards a climatology of stratospheric bromine monoxide from SCIAMACHY limb observations

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Abstract

Retrievals of stratospheric bromine monoxide (BrO) profiles from two years of limb measurements from the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) instrument onboard ENVISAT are analysed and a global climatology of stratospheric BrO is prepared. A comparison of the SCIAMACHY BrO retrievals with a set of four balloon-borne BrO profiles shows mean relative differences in the altitude range from 18 to 30 km between +17% and −42%. The SCIAMACHY BrO observations provide for the first time a picture of the seasonal variation of stratospheric BrO on a global scale. At mid-latitudes of both hemispheres BrO shows a strong seasonal cycle with a maximum in winter and a minimum in summer. The seasonal variation of BrO is closely correlated with changes in nitrogen dioxide (NO_2), confirming our present understanding of gas phase bromine chemistry. Using the SCIAMACHY BrO observations together with the calculated bromine partitioning from a photochemical model constrained by the SCIAMACHY NO_2 observations, the total stratospheric bromine loading is estimated to be 18.5±4 pptv. This indicates a contribution of about 3.5±4 pptv from short lived bromine species in addition to methyl bromide and the halons.

1 Introduction

Halogen compounds containing chlorine and bromine play a dominant role in the depletion of stratospheric ozone. Inorganic bromine compounds have a potential to cause far greater ozone losses at per molecule level than their chlorine counterparts. Despite their important role in the ozone destruction process, there are very few measurements of inorganic bromine species in the stratosphere. $BrONO_2$ and BrCl have never been measured. There exist only few measurements of HBr and only upper limit measurements of HOBr in the stratosphere (Johnson et al., 1995; Nolt, 1997). The only major inorganic bromine compound that has been measured previously in the stratosphere

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is bromine monoxide (BrO).

BrO has been measured in-situ by resonance fluorescence spectroscopy from both aircraft (Brune et al., 1989; Toohey et al., 1990; Avallone et al., 1995) and balloon (McKinney et al., 1997). BrO profiles have also been measured from balloon borne UV-visible spectroscopy (Pundt et al., 2002; Harder et al., 1998; Dorf et al., 2005). Ground based UV-visible spectroscopy (Carroll et al., 1989; Solomon et al., 1989; Fish et al., 1997; Richter et al., 1999; Otten et al., 1998; Frieß et al., 1999; Sinnhuber et al., 2002; Schofield et al., 2004) has been used to measure BrO slant column densities. BrO column density measurements have also been done from space by the Global Ozone Monitoring Experiment (GOME) instrument (e.g., Wagner and Platt, 1998; Richter et al., 2002). SCIAMACHY onboard ENVISAT provides the first global observations of stratospheric BrO profiles. First results of SCIAMACHY BrO observations for a 10 day period in September 2002 have been reported by Sinnhuber et al. (2005). Here we present now an analysis of the SCIAMACHY BrO observations over a period of two years which allows a first global view on the seasonal variation of stratospheric BrO.

The paper is organised in the following way. Section 2 reviews briefly our present understanding of the stratospheric bromine chemistry. In Sect. 3, our BrO retrieval method is presented along with sensitivity studies. In order to validate our SCIAMACHY BrO retrievals, a first comparison with balloon-borne BrO profiles is performed. Section 4 introduces the photochemical model used in this study along with a discussion on the partitioning of bromine species obtained from the 1-D model. Section 5 discusses the results of the two years of BrO climatology. Section 6 presents our estimate of the stratospheric Br_y (calculated using the inorganic method) and the total bromine loading. Finally conclusion is given in Sect. 7.

2 Stratospheric Bromine Chemistry

The primary sources of bromine in the stratosphere are natural and anthropogenic methyl bromide and anthropogenically produced halons released at the Earth's surface. Very short lived bromine substances (VSLS) like CH_2Br_2 and CH_2BrCl also contribute to the stratospheric bromine loading. It has also been proposed that another short lived bromine species namely bromoform ($CHBr_3$) could make a contribution of up to 1 pptv to stratospheric bromine (Dvortsov et al., 1999; Sturges et al., 2000; Nielsen and Douglass, 2001; Sinnhuber and Folkins, 2005). Volcanic plumes could also make a contribution to the stratospheric bromine (Bobrowski et al., 2003). However the contribution of volcanic eruptions to the stratospheric bromine is unclear at present. Afe et al. (2004), using retrievals from GOME and SCIAMACHY, found no indications of enhanced BrO during volcanic eruptions. The organic sources of bromine are converted to inorganic forms (Br_y=Br, BrO, $BrONO_2$, HOBr, HBr, BrCl) by photolysis or reactions with OH radicals at higher altitudes in the troposphere and stratosphere which then subsequently participate in ozone destruction cycles. Br and BrO are called as reactive species while $BrONO_2$, HOBr, HBr and BrCl are called as reservoir species. These inorganic bromine species participate in the catalytic destruction of ozone.

An important but still unresolved question is the total bromine loading in the stratosphere. Accurate information of the total bromine in the stratosphere is important to evaluate bromine catalysed destruction of the stratospheric ozone. The Br_y in the stratosphere can be estimated indirectly from the measurements of organic source gases in the stratosphere (organic method) (Schauffler et al., 1998; Wamsley et al., 1998) or by using the stratospheric BrO measurements along with a modeled BrO/Br_y ratio (Pfeilsticker et al., 2000; Harder et al., 2000; Sinnhuber et al., 2002, 2005) (inorganic method). For early 1999, for example, the estimated volume mixing ratio of total bromine at 25 km in air of 5.6-year mean age was 18.4 (+1.8,−1.5) pptv based on the organic method and 21.5±3 pptv using the inorganic method (WMO, 2002, Figs. 3–26). The offset in the two methods allows for a possibility of a contribution of around

3.1 (−2.9, +3.5) pptv from VSLS.

The most abundant inorganic bromine species in the stratosphere during the daytime is BrO. Photochemical models have shown that it forms around 40–70% of Br_y (e.g., Lary et al., 1996a; Sinnhuber et al., 2002). The primary source of BrO in the stratosphere is the reaction

$$Br + O_3 \rightarrow BrO + O_2. \quad (1)$$

Other sources of BrO include photolysis of reservoir species like $BrONO_2$ or reaction of $O(^3P)$ with reservoir species like $BrONO_2$ (Soller et al., 2001; Sinnhuber et al., 2002, 2005) or HOBr. The main sinks of BrO in the stratosphere are photolysis, reaction with $O(^3P)$, and reaction with NO. The reaction of BrO with ClO is also an important sink of BrO and also an important reaction for catalytic ozone destruction.

Among the reservoir bromine species, the most abundant species in the stratosphere during the daytime is $BrONO_2$ which is formed by a three-body reaction

$$BrO + NO_2 + M \rightarrow BrONO_2 + M. \quad (2)$$

Photolysis of $BrONO_2$ releases BrO back into the atmosphere. Thus, $BrONO_2$ is very close to a photochemical steady state during the daytime. $BrONO_2$ is believed to account for nearly half of Br_y in the lower stratosphere during the daytime. The sink of $BrONO_2$ during the daytime is photolysis or reaction of $O(^3P)$. The major nighttime loss of $BrONO_2$ is through hydrolysis. Erle et al. (1998) have shown that hydrolysis of $BrONO_2$ on cold stratospheric aerosols can be an important source of halogen activation. Also it influences HO_x and NO_x concentrations which has significant effect on ozone depletion (Lary, 1996b).

The hydrolysis of $BrONO_2$ sulfate aerosols is also a source of HOBr (Lary et al., 1996a). Another important source of HOBr is the reaction of BrO with HO_2. The destruction of HOBr is through photolysis, which causes rapid increase of HO_x during sunrise. HOBr is also destroyed through reaction with $O(^3P)$.

HBr is the longest lived reservoir species. HBr forms only a small fraction of Br_y in the stratosphere. The sources of HBr are the reaction of Br with HO_2 and the reaction with formaldehyde (HCHO) (Lary et al., 1996a). A possible minor channel of source of HBr also exists through the reaction of BrO with HO_2 (Lary et al., 1996a). Photochemical models which included 0-2% production of HBr through the reaction of BrO with HO_2 have been found to be in good agreement with field measurements (Johnson et al., 1995). The important sinks of HBr are reactions with OH and $O(^3P)$.

During the period of chlorine activation BrCl may become an important reservoir species through the reaction

$$BrO + ClO \rightarrow BrCl + O_2. \quad (3)$$

In fact this is the smallest of the three channels which exists in the reaction of BrO and ClO. The other two channels of the reaction of BrO and ClO result in the formation of (a) OClO+Br (yield is 59%) and (b) ClOO+Br (yield is 34%). The channel mentioned in Reaction (3) produces 7% yield of BrCl and O_2. The yields mentioned are observed at 195 K using JPL 2002 kinetics (Sander et al., 2003; Canty et al., 2005). During the daytime BrCl photolyses very quickly to produce Br.

3 SCIAMACHY BrO observations

The SCIAMACHY instrument (Bovensmann et al., 1999) onboard ENVISAT was launched in March, 2002. ENVISAT flies in a sun synchronous low polar orbit with equator crossing time of about 10 LT. SCIAMACHY measures sunlight transmitted through the Earth's atmosphere or reflected and scattered by the Earth's atmosphere and surface in the spectral range of 240–2380 nm. The scattered and reflected spectral radiance is measured in nadir and limb geometry, while spectral radiance transmitted through the atmosphere is measured in solar or lunar occultation mode. The combination of nadir and limb measurements can be used to retrieve the tropospheric

concentration of atmospheric trace gases. A detailed description of the instrument and its capabilities is given by Bovensmann et al. (1999).

BrO columns are retrieved from the nadir measurements, while the BrO profiles from the the limb measurements of SCIAMACHY. In this work the limb retrieval of BrO (Rozanov et al., 2005a) are used.

3.1 Retrieval of BrO profiles from SCIAMACHY limb observations

Vertical distributions of BrO are retrieved from the SCIAMACHY limb measurements using the spectral information in the 337–357 nm wavelength interval. The forward simulations of the SCIAMACHY limb measurements as well as the calculations of the appropriate weighting functions are done employing the SCIATRAN radiative transfer model (Rozanov, 2004; Rozanov et al., 2005b). In the spherical mode the SCIATRAN model calculates the limb radiance properly considering the single scattered radiance and using an approximation to account for the multiple scattering. To improve the retrieval quality, vertical profiles of O_3 and NO_2 are estimated in combination with BrO retrievals using the same spectral information. Limb measurements performed at tangent heights from 12 to 30 km are considered. To reduce the impact of the Fraunhofer structure and incorrect instrument calibration all selected limb scans are divided by the reference limb measurement obtained at a tangent height of about 33 km. To account for broadband features resulting from unknown scattering properties of the atmosphere as well as instrument calibration issues, a cubic polynomial is subtracted from all spectral ratios and weighting functions.

The forward model is initialized using a climatological data base (C.A. McLinden, Personal communications), a background aerosol loading according to the LOWTRAN aerosol parameterization (Kneizys et al., 1996), a surface albedo of 0.3, temperature dependent absorption cross sections of O_3, NO_2 and BrO, and the O_4 cross section from Greenblatt et al. (1990). The cross sections of O_3 and NO_2 were measured by the SCIAMACHY Proto Flight Model (PFM) Satellite Spectrometer (Bogumil et al., 1999) and the BrO cross sections were obtained by the time-resolved rapid scan Fourier

Transform Spectroscopy (FTS) method (Fleischmann et al., 2004) and then convolved to the SCIAMACHY resolution assuming the Gaussian form of the instrument slit function. The absorption cross section, which are used in the SCIAMACHY BrO limb retrievals have an accuracy of 10–20% (Fleischmann et al., 2004).

The retrieval of BrO profiles is performed as described by Rozanov et al. (2005a) using a two-step retrieval procedure. At the preprocessing step, which is done for each tangent height independently, a possible misalignment of the wavelength grids of the limb spectra, of the reference spectrum, and of the forward model is accounted for. Additionally, known corrections, namely, the ring and tilt spectra, as well as instrument calibration functions, are applied. The main retrieval step is based on the solution of the linearized forward equation given by

$$\boldsymbol{y} = \boldsymbol{K}\,\boldsymbol{x} + \epsilon\,. \tag{4}$$

Here, the measurement vector, $\boldsymbol{y}$, contains the differences between ratios of simulated and measured differential limb spectra at all tangent heights selected for the retrieval with all corrections from the preprocessing step applied, the state vector, $\boldsymbol{x}$, contains relative differences of trace gas number densities (with respect to the initial values) at all altitude layers for all gases to be retrieved, and ϵ denotes errors of any kind (e.g., measurement noise, linearization error, etc.). The linearized forward model operator, $\boldsymbol{K}$ comprises of appropriate weighting functions. The final solution is found iteratively employing the optimal estimation technique (Rodgers, 2000). Since no reliable statistical information on the vertical distribution of BrO is available, the Levenberg-Marquard iteration type (Dennis and Schnabel, 1983; Hanke, 1997) is employed replacing the a priori information at each iteration step by the results obtained at the previous iteration.

3.2 Sensitivity studies

In this section the dependence of the retrieved vertical profiles of BrO on the assumed atmospheric composition, surface reflection, and measurement geometry parameters

is investigated. This is done for a selected limb measurement performed on 3 July 2004 in the tropical region. The vertical profile of BrO obtained using the standard input for the forward model and the retrieval algorithm is treated as the reference. The vertical distributions retrieved using perturbed input parameters provide an estimate of the sensitivity of the retrieval to the corresponding parameter.

The influence of atmospheric composition parameters such as pressure, temperature, and aerosol loading as well as of the surface reflection on the retrieved BrO mixing ratios is presented in Fig. 1. The reference vertical distribution of BrO obtained using the standard settings in the forward model and in the retrieval algorithm is shown by the solid line. Other curves in the left panel in Fig. 1 depict the BrO volume mixing ratio profiles obtained for the perturbed input parameters. The shaded area represents the total estimated uncertainty of the retrieved profile. The right panel shows the relative differences of the corresponding profiles with respect to the reference (i.e., "unperturbed") profile. As seen from the plot, the largest influence on the retrieved BrO profile is due to the change in the temperature profile. For example, a decrease in the temperature by 10 K results in a relative deviation in BrO mixing ratio of up to 60% in the lower stratosphere and up to 42% at higher altitude (shown by the dot-dashed line with pluses in the plot). However, it is worth mentioning that despite relatively high relative values, the absolute deviation in the retrieved BrO volume mixing ratio due to the change in the temperature profile by 10 K is always less than 0.5 pptv below 23 km. The dependence of the retrieved profiles on the temperature is most probably due to the temperature dependent cross sections, mostly of ozone, used in the forward model. The second largest influence on retrieved BrO profiles demonstrates the changes in the scattering properties of the atmosphere which may be caused by the changes in the pressure or aerosol loading. Thus, a decrease in pressure by 10% (dot-dot-dashed line with squares) and a reduction of scattering events in a pure Rayleigh atmosphere (dot-dot-dot-dashed line with crosses) result in nearly the same relative deviations in the retrieved BrO profile of up to 20% whereas an increased stratospheric aerosol loading simulated using the moderate volcanic aerosol instead of background according to the

LOWTRAN aerosol parameterization (dashed line with diamonds) causes a relative deviation of nearly the same amount with an opposite sign. Illustrating a weak sensitivity of the employed method to the optical properties of the surface, the relative deviation in the retrieved BrO caused by the increase of the surface albedo to 0.9 remains always below 10% (dotted line with triangles).

One of the main issues for all limb scattering instruments is the accuracy with which the tangent heights can be determined (von Savigny et al., 2004). Already in the early stage of the SCIAMACHY mission, a substantial error in the SCIAMACHY pointing as provided by ESA was identified. We studied the effect of wrong tangent height alignment on the retrieval of the SCIAMACHY BrO.

Figure 2 illustrates the influence of the instrument mispointing on the retrieved BrO profiles. The presentation form here is similar to Fig. 1. The perturbed profiles are obtained associating the limb measurements to "wrong" values of the tangent height and then running the forward model and the retrieval. All tangent height values are changed by the same amount simulating a constant shift in the tangent height alignment. Negative values for the tangent height shift denote that the assumed tangent height grid is shifted downwards with respect to the original one. Afterwards the retrieved BrO number density profiles are shifted back by the mispointing amount and converted into the volume mixing ratios. This is done to simulate the post-processing pointing correction as it is applied to BrO profiles. As seen from the plot, the resulting error in BrO volume mixing ratio profiles due to 1 km mispointing is 10–20% above 21 km increasing to about 40% in the lower layers.

Figure 3 illustrates the influence of a priori information used in the forward model and in the retrieval algorithm on the retrieved BrO volume mixing ratio profiles. In the left panel BrO volume mixing ratio retrieved assuming different a priori profiles is shown by curves with symbols. Corresponding a priori profiles are shown by the lines of the same type without symbols. Solid line depicts the standard retrieval. Due to decreasing information content of the limb measurements the largest impact of a priori information is expected in the lower stratosphere. Since the absolute values of BrO mixing ratio in

this altitude region are low, it is more convenient to show absolute differences in the BrO profile as presented in the right panel of Fig. 3. As seen from the plot, differences in BrO volume mixing ratio caused by the usage of different a priori profiles are typically within 0.6 pptv.

3.3 Comparison with balloon-borne BrO profile measurements

As a first step towards a validation of our SCIAMACHY BrO retrievals we compare our BrO profiles with the set of balloon-borne BrO measurements compiled by Dorf et al. (2005). Due to the diurnal variation of BrO it is necessary to include a photochemical correction of the measured BrO profiles that takes into account the differences in the time of day (and thus solar zenith angles) between the two measurements (for more details see Dorf et al., 2005). Forward and backward trajectories are started at the location of the balloon measurements and used to find optimal matches with SCIAMACHY profiles (Dorf et al., 2005). For two of the four balloon profiles forward and backward matches are available, for the other two only forward matches.

The relatively large statistical error of about 30% for individual SCIAMACHY BrO profiles makes it difficult to detect possible systematic differences when comparing individual profiles. Therefore we have also included the SCIAMACHY monthly mean BrO profiles for the corresponding latitude band in the comparison.

Figure 4 shows the comparison between the measured BrO profile from a TRIPLE flight conducted on 24 September 2002 at Aire sur l'Adour, France (44°N) with the SCIAMACHY BrO limb retrieval. As the TRIPLE flight was close in time to the SCIAMACHY overpass no photochemical correction was needed in this case. Figures 5 and 6 show the comparison with a DOAS flight on 23 March 2003 in Kiruna (68° N) and with a DOAS flight on 9 October 2003 at Aire sur l'Adour. Figure 7 shows the comparison with a SAOZ flight at Bauru, Brazil (22° S) on 31 January 2004. For further information about the measurement techniques, photochemical correction of BrO profiles, and forward and backward trajectory mapping the reader is referred to Dorf et al. (2005).

The mean relative differences over the altitude range from 18 to 30 km are +17%

for the September 2002 TRIPLE flight at Aire sur l'Adour, +14% for the March 2003 DOAS flight, −20% and −29% for the two matches of the October 2003 DOAS flight at Aire sur l'Adour, and −32% and −42% for the two matches of the January 2004 SAOZ flight at Bauru. Below 20 km our retrievals show very low amounts of BrO while the SAOZ profile shows much higher BrO mixing ratios between 2 and 5 pptv. A comparison with first results from in-situ BrO measurements in the tropics (F. Stroh, personal communication, 2006) and the first DOAS BrO profile in the tropics (Dorf, 2005) show lower amounts of BrO below 20 km as compared to the SAOZ profile and appear to be in better agreement with our SCIAMACHY BrO retrievals. Although it is difficult to be fully conclusive at this stage because of the large differences between the comparisons for the different balloon flights, the agreement between SCIAMACHY and the photochemically corrected balloon-borne BrO profiles is encouraging, in particular at mid-latitudes.

Dorf et al. (2005) have presented a comparison with SCIAMACHY BrO retrievals performed with the Harvard Smithsonian algorithm (Sioris et al., 2006). The Harvard BrO retrievals seem to be systematically higher compared to our BrO retrievals, at least for the few profiles shown. The reason for this discrepancy is still unclear and will be investigated in an intercomparison project that was initiated recently.

4 Photochemical modeling of the BrO diurnal variation

4.1 Model

The 1-D model is based on the photochemical scheme from the SLIMCAT model (Chipperfield, 1999). The model contains a detailed stratospheric chemistry which includes gas phase as well as heterogeneous reactions. In all, there are 135 chemical reactions and 44 photolysis reactions of 52 species which are considered to be important for the stratospheric chemistry. The model is initialised with the output from a 2-D chemistry, transport and radiation model, which is a composite of the SLIMCAT chemistry (Chip-

perfield, 1999; Sinnhuber et al., 2003) and the THIN AIR dynamics code (Kinnersley, 1996). Temperature and pressure in the model are taken from ECMWF analysis. The reaction rate constants and photolysis cross sections are taken from the latest JPL-2002 recommendations (Sander et al., 2003). As mentioned previously the reaction of $BrONO_2$ with $O(^3P)$ (Soller et al., 2001) could be an important source of BrO at higher altitudes (Sinnhuber et al., 2005). This reaction has not been considered in the JPL 2002 catalogue. However, we have included this reaction in our model simulations.

To estimate Br_y in the stratosphere using the inorganic method, it is important to have a realistic partitioning of bromine species in the model. Since bromine partitioning is controlled by NO_2 (Fish et al., 1997; Richter et al., 1999), the 1-D model used in this study is constrained by the SCIAMACHY NO_2 profiles by scaling NO, NO_2, NO_3, and HNO_3 (but not $ClONO_2$ and BrONO2!) in the initialization until the modeled NO_2 agrees with measured NO_2 at the local time of the SCIAMACHY measurements. The model is run for a period of 5 days in order to allow for spin up and all calculations are done using the output of the fifth day.

4.2 Bromine partitioning

Figure 8 shows the bromine partitioning for the four seasons and five latitude zones. In general it is observed that BrO and $BrONO_2$ form a major part of the daytime Br_y. Other reservoir species like HBr, HOBr, BrCl form a very small fraction of Br_y. The model calculations show that BrO is on an average 40–70% of Br_y, consistent with previous studies (Sinnhuber et al., 2002; Pundt et al., 2002). Avallone et al. (1995) compared model calculations of the BrO/Br_y ratio in the northern hemisphere lower stratosphere with in situ airborne observations. While their modeled BrO/Br_y ratio was around 50–60%, comparable to our results, the observations suggested a much smaller BrO/Br_y ratio of only about 40%. The reason for the discrepancy between their observed and modeled BrO/Br_y is still not clear.

During high-latitude winter (December–January–February in the Arctic and June–July–August in the Antarctic) BrO is around 75% and $BrONO_2$ forms only a small

fraction of Br_y. This is due to the very low levels of NO_x in this region and further demonstrates the role of NO_x in bromine partitioning. In the tropics, the partitioning of bromine species is similar to the other zones in the upper stratosphere. However in the lowermost stratosphere and in the uppermost troposphere, it is found that HBr and Br form 10–40% of Br_y while the concentration of $BrONO_2$ is between 10–20% as against around 40% in the upper stratosphere. The reaction of Br with HO_2 is a source of HBr while the reaction of Br with ozone is an important sink of Br. The VMR of ozone is significantly low in the tropopause and the uppermost troposphere as compared to the stratospheric values. This results in Br and HBr forming a larger fraction of Br_y. NO_2 does not appear to play a significant role in bromine partitioning in the lowermost stratosphere in the tropics. Antarctic winter is the only region where a significant amount of BrCl is predicted by the model. Under these conditions the model predicts also enhanced levels of HOBr.

As these model calculations are constrained by NO_2 from SCIAMACHY observations, the results depend to some extent on the accuracy of the SCIAMACHY NO_2 observations. In order to check the effect of changes in NO_2 on BrO/Br_y ratio, we conducted some sensitivity tests. An increase in NO_2 concentration results in an increase in $BrONO_2$ concentration through the Reaction (2). Consequently, this results in a decrease in BrO. The change in $BrONO_2$ and BrO is altitude dependent due to the pressure dependent nature of Reaction (2). On an average it is found that if we increase the NO_2 concentration by 50% then BrO decreases by approximately 11% at altitudes of around 25 km. Thus the BrO/Br_y ratio would decrease by 11%. The statistical results from the comparison of all SCIAMACHY with Halogen Occultation Experiment instrument (HALOE) collocated NO_2 profiles show a systematic negative offset of less than 5% between 20 km and 38 km (Bracher et al., 2004, ; A. Bracher, personal communication, 2005). This 5% bias in NO_2 leads only to a bias in the calculated BrO/Br_y ratio of about 1% which is negligible compared to other potential error sources.

5 BrO climatology and the seasonal variation of BrO

A global seasonal climatology of stratospheric BrO is prepared from SCIAMACHY measurements during the years 2003 and 2004. However, data were not available for May, June, and July 2003 due to a change in the measurement mode of SCIAMACHY during this period. This means that the climatology is based so far on observations from 21 months.

The area weighted monthly mean profiles are calculated over five latitude bands: The Arctic (north of 60° N), northern hemisphere mid-latitudes (30° N–60° N), tropics (30° S–30° N), southern hemisphere mid-latitudes (30° S–60° S), and the Antarctic (south of 60° S). Prior to this, the tangent height (TH) corrections are applied to the monthly averaged profiles using the TH offsets given in Table 1 of von Savigny et al. (2005). Note that due to the inability of the instrument to measure in darkness, data are not available above 75° N in November, above 70° N in December and above 75° N in January. Similarly the data are not available above 70° S in May, above 65° S in June, and above 70° S in July. The seasonal averages are calculated according to the availability of the monthly zonal means. Temperature and pressure profiles needed to convert the BrO number densities to volume mixing ratios are taken from ECMWF.

On an average there are approximately 130 profiles per 5° latitude bin per month. In calculating the seasonal zonal averages for two years, approximately 90 000 profiles are used. The calculated seasonal means presented here, are interpolated to a common altitude grid for a better comparison.

Figure 9 shows the seasonal and zonal climatology of SCIAMACHY BrO between 15 and 28 km. BrO VMRs increase with altitude at all latitudes mainly due to the dissociation of the organic bromine source species (Wamsley et al., 1998). During December–January–February (DJF) in the northern hemisphere (NH), BrO VMRs are larger at higher latitudes and altitudes as compared to the corresponding latitudes and altitudes in the southern hemisphere (SH). During March–April–May (MAM) BrO VMRs appear to be increasing at higher latitudes in the SH and during June-July-August (JJA) the

scenario is opposite to that during DJF. During September–October–November (SON) again the increase in BrO VMRs NH higher latitudes is observed.

The seasonal variation of BrO will in general be a result of changes in Br_y due to transport and changes in the bromine partitioning due to chemistry. It is expected that the BrO/Br_y ratio will show a seasonal variation anti-correlated to the seasonal cycle of NO_2: A rise in NO_2 concentration will result in the rise in $BrONO_2$ and consequently in the decrease in BrO (Fish et al., 1995). It is thus interesting to test, to what extent the observed seasonal variation of BrO can be explained by the seasonal cycle of NO_2. Figures 10a, c, and e show the annual variation of BrO at 24 km in northern mid-latitudes, the tropics and southern mid-latitudes, respectively for the year 2004. A strong annual variation of BrO at mid-latitudes of both hemispheres is evident, with a maximum in winter and a minimum in summer. The amplitude of the seasonal cycle of BrO at 24 km in the northern hemisphere is larger than in the southern hemisphere. Figures 10b, d and f show that the annual variation of BrO is closely anti-correlated with the NO_2 concentrations, measured simultaneously by SCIAMACHY. The variation of BrO is qualitatively similar to the one addressed previously by Richter et al. (1999) over Bremen (53° N). A comparison with the photochemical model shows that in the NH the change in BrO is larger than expected from changes in NO_2 alone. This could mean that either other processes, in particular transport, contribute to the seasonal variation of BrO or current photochemistry underestimates the sensitivity of BrO to changes in NO_2. However, since the BrO observations in the southern hemisphere do not show a higher sensitivity to changes in NO_2 when compared to the model, this would argue against a chemical explanation and suggests that transport contributes to the observed BrO changes. Both NO_2 and BrO show only little seasonal variation in the tropical lower stratosphere.

Figure 11 shows the comparison of seasonally and zonally averaged profiles of BrO VMRs of the two years. DJF and SON are the only seasons where the seasonal and zonal mean BrO VMRs for the two years can be compared for all the latitude bands as the number of months used to calculate the seasonal average is same. The

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shapes of the BrO profiles for the same season and zone of the corresponding years (i.e. 2003 and 2004) are qualitatively consistent with each other. In general, we find that for all seasons and zones BrO VMR increases steadily with altitude and reaches peak values around 20–24 km and then remains constant between 9–14 pptv up to the highest altitude. The averaged profiles are also qualitatively consistent with previously published work on BrO (Brune et al., 1989; Harder et al., 1998; Woyke et al., 1999; Toohey et al., 1990; Pundt et al., 2002).

In most cases, the seasonal mean BrO VMRs during 2003 are consistently larger than those during 2004. The tangent height offset applied during the two years may contribute partly to this observed discrepancy. Also, a part of the larger discrepancy observed during MAM and JJA could be explained by the different number of months considered in calculating the seasonal averages in 2003 and 2004.

6 Inferred Br_y and the total bromine loading

We have estimated Br_y (by the so called inorganic method), using SCIAMACHY BrO measurements and the calculated BrO/Br_y ratio from the photochemical model, constrained by the SCIAMACHY NO_2 observations. Figure 11 shows the profiles of Br_y for the two years 2003 and 2004. The mean total stratospheric bromine loading (Br_{total}^{mean}) can be estimated by summing the calculated Br_y and the estimate for the contribution of remaining organic bromine compounds. Based on CFC-11 observations in September 2002 from the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) also onboard ENVISAT (Glatthor et al., 2005) and the empirical relationship of Wamsley et al. (1998), we have estimated the average organic bromine in the extra-tropics to be 0.77 pptv at 24 km and 0.15 pptv at 27 km (see also Sinnhuber et al., 2005). The calculated extra-tropical Br_y from SCIAMACHY BrO is on average 18.03 pptv at 24 km and 17.98 pptv at 27 km. Using the average organic bromine at 24 and 27 km for September 2002 (as representative of the whole year to a first approximation) and the average value of estimated Br_y at the same altitudes, the mean total bromine loading in the

stratosphere around 25 km (Br_{total}^{mean}) is found to be 18.5 pptv. Assuming an accuracy of about 20% for the SCIAMACHY BrO profile retrievals the uncertainty in Br_{total}^{mean} will be about ±3.7 pptv.

This estimate of Br_{total}^{mean} is consistent (albeit with higher uncertainty) with the works of Schauffler et al. (1998), who calculated the total organic bromine loading at the tropical tropopause to be 17.4±0.9 using the organic method which included 3 short lived species namely CH_2Br_2, CH_2BrCl, and $CHCl_2Br$ apart from CH_3Br and halons. The calculated value is also consistent with works of Wamsley et al. (1998) (which ranged from (16.4±2 pptv) in 6 year old air investigated in 1994 to (18.2±2) in 0 year old air) using organic method which included CH_3Br, halons and two short lived species namely CH_2Br_2 and CH_2BrCl and that of Pfeilsticker et al. (2000) who estimated for early 1999, the total organic bromine at 25 km in air of 5.6 year mean age to be 18.4 (+1.8/−1.5) pptv from organic precursor measurements which included all known major organic bromine species.

However, the estimated value of total bromine loading in this work is on the lower side (though within stated error of measurements) as compared to previous works which calculated the total bromine loading using BrO measurements and known BrO/Br_y from the model e.g. the work of Pfeilsticker et al. (2000) who estimated inorganic bromine loading of 21.5±3 pptv for air of 5.6 year mean age for winter 1998/99, Harder et al. (2000) (20±2.5) and of Sinnhuber et al. (2002) (20±4 pptv). The inclusion of the reaction proposed by Soller et al. (2001) decreases the gap between between this work and that of Pfeilsticker et al. (2000), Harder et al. (2000).

The major contribution to the bromine in the stratosphere is from CH_3Br, Halon-1211 and Halon-1301 (Wamsley et al., 1998; Pfeilsticker et al., 2000) and this sums up to 15 pptv (Sinnhuber et al., 2005). The total bromine loading of 18.5±4 pptv estimated in this work indicates a contribution of 3.5±4 pptv from short lived to stratospheric bromine loading in addition to that from CH_3Br and halons in agreement with previous studies (Pfeilsticker et al., 2000; Sinnhuber et al., 2002, 2005; Salawitch et al., 2005).

7 Conclusions

We present a first global climatology of stratospheric BrO, based on retrievals from two years of measurements of the SCIAMACHY satellite instrument. A comparison of the SCIAMACHY BrO retrievals with a set of balloon-borne BrO measurements shows mean differences in the altitude region from 18 to 30 km between +17% and −29% at mid and high latitudes of the northern hemisphere. Larger discrepancies of −32% and −42% are found in comparison to a SAOZ balloon profile in the tropics.

BrO shows a strong annual variation at mid-latitudes while there is no significant annual variation in the tropics. The seasonal variation at mid-latitudes is inversely correlated with NO_2, confirming our present understanding of the gas phase bromine chemistry.

The total bromine loading is estimated from the BrO observations using the inorganic method. The total bromine loading is 18.5±4 pptv consistent with previously published results (Schauffler et al., 1998; Wamsley et al., 1998; Pfeilsticker et al., 2000; Harder et al., 2000; Sinnhuber et al., 2002; WMO, 2002). Our estimate is slightly on the lower side (though within the stated error estimates) as compared to the estimates of (Pfeilsticker et al., 2000; Harder et al., 2000). Part of the difference can be explained by the inclusion of the reaction of $BrONO_2$ with $O(^3P)$ (Soller et al., 2001). The total bromine loading of 18.5±4 pptv suggests a contribution of 3.5±4 pptv from short lived organic bromine compounds in addition to methyl bromide and the halons.

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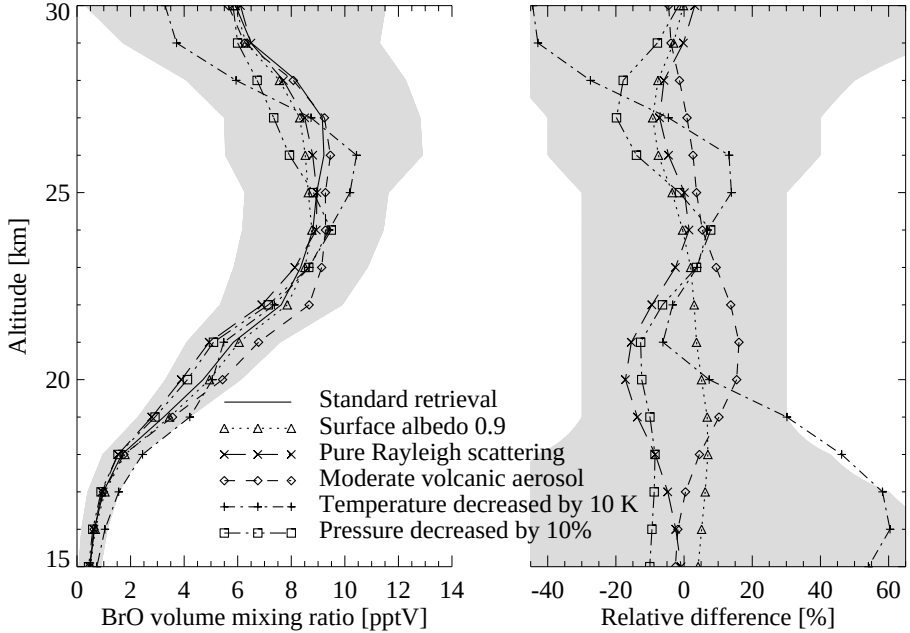

Fig. 1. Dependence of the retrieved vertical distribution of BrO on the atmospheric composition and surface properties. Left panel: BrO volume mixing ratio retrieved assuming different input parameters. Right panel: Relative differences of BrO profiles obtained using perturbed input parameters with respect to the standard retrieval. The shaded area represents the total estimated uncertainty of the retrieved profile.

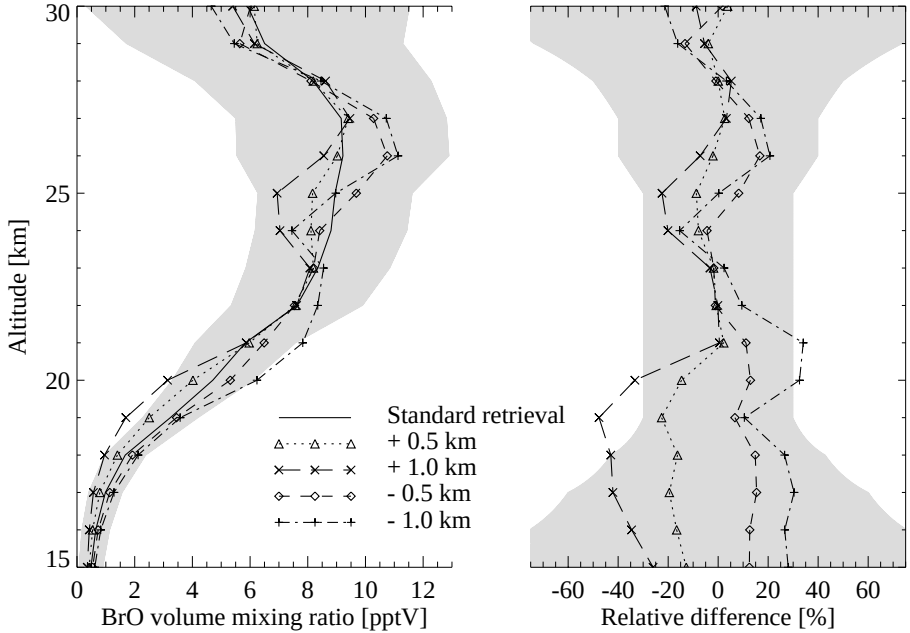

Fig. 2. Influence of the instrument mispointing on the retrieved vertical distribution of BrO. Left panel: BrO volume mixing ratio retrieved assuming different pointing corrections. Right panel: Relative differences of BrO profiles obtained using pointing corrections with respect to the standard retrieval.

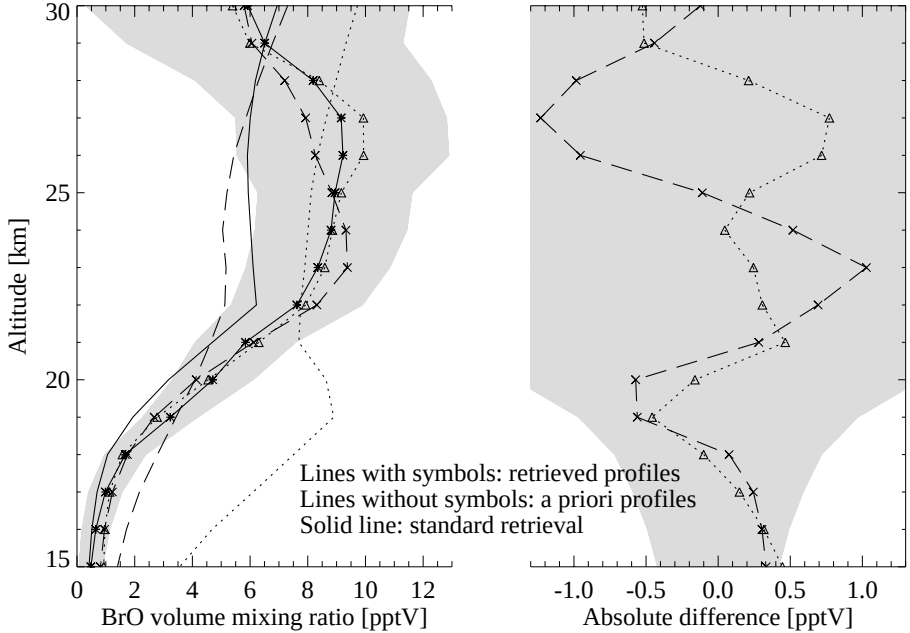

Fig. 3. Influence of a priori information on the retrieved vertical distribution of BrO. Left panel: Curves with symbols show BrO volume mixing ratio retrieved assuming different a priori profiles shown by the lines of the same type without symbols. Solid line depicts the standard retrieval. Right panel: Absolute differences of BrO profiles obtained using different a priori profiles with respect to the standard retrieval.

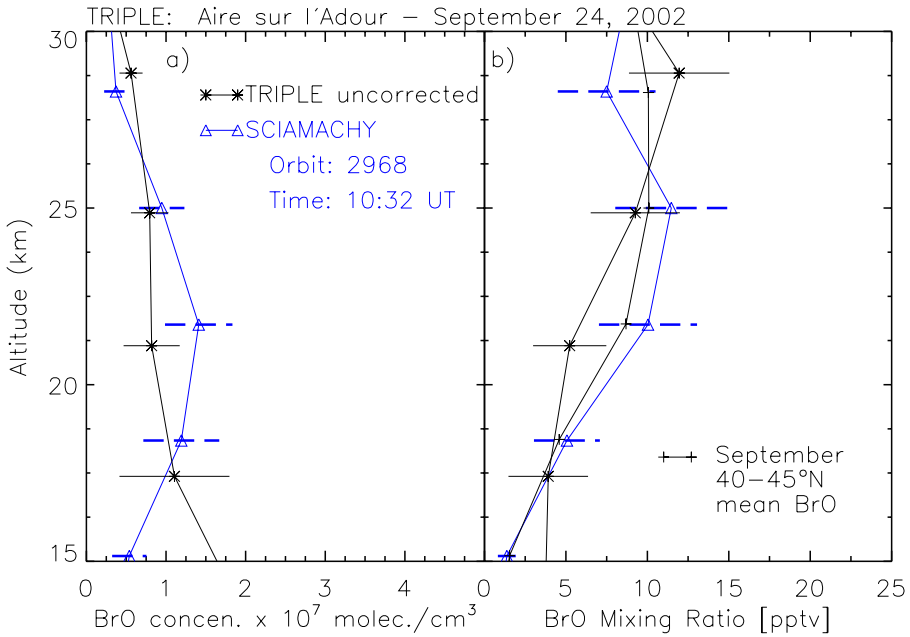

Fig. 4. Comparison of SCIAMACHY BrO retrievals with balloon-borne BrO observations from the TRIPLE instrument. **(a)** BrO number density profiles from the TRIPLE flight on 24 September 2002 from Aire sur l'Adure (43.7° N, balloon SZA=60.1° (a.m.)), together with the corresponding SCIAMACHY profile from Orbit 2968. The retrieval error is approximately 40% between 15–20 km and 25–30 km, while it is 30% between 20–25 km. **(b)** as in panel (a) but expressed as volume mixing ratio. In addition, the corresponding monthly mean profile from SCIAMACHY for the range from 40° N to 45° N is shown.

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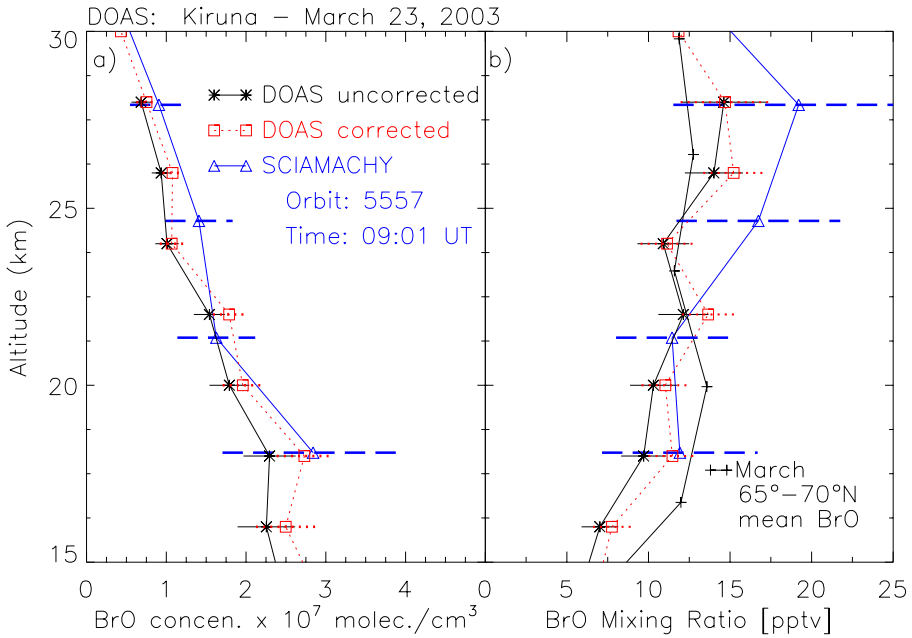

Fig. 5. Same as Fig. 4 but for a comparison with the DOAS balloon flight on 23 March 2003 from Kiruna (67.9° N, balloon SZA=80° (p.m.)). In addition to the measured BrO profile from the DOAS instrument also a photochemically corrected profile is shown.

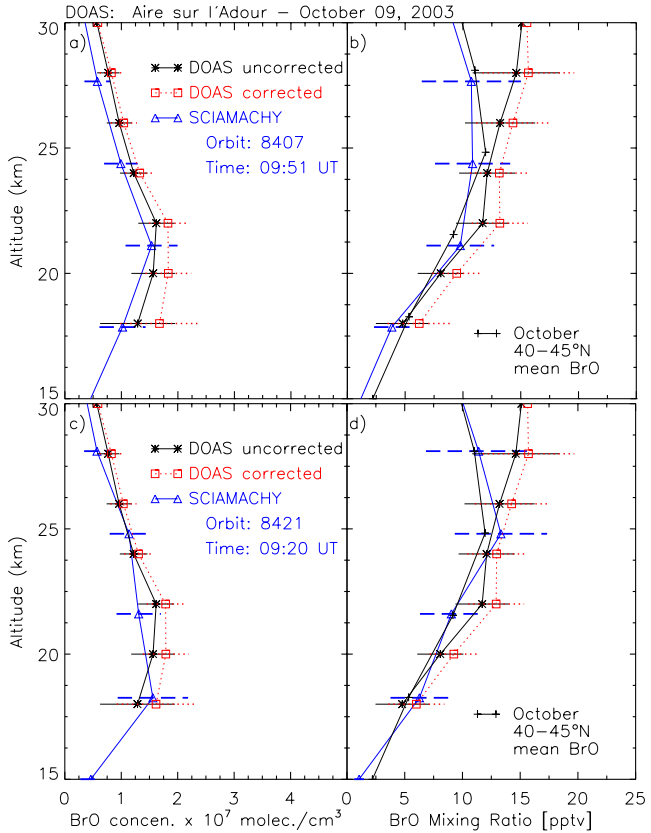

Fig. 6. Same as Fig. 5 but for a comparison with the DOAS balloon flight on 9 October 2003 from Aire sur l'Adure (43.7° N, balloon SZA=72.9° (p.m.)). Panels **(a)** and **(b)** show a backward trajectory match, while panels **(c)** and **(d)** show a forward trajectory match. See text for details on the trajectory matches.

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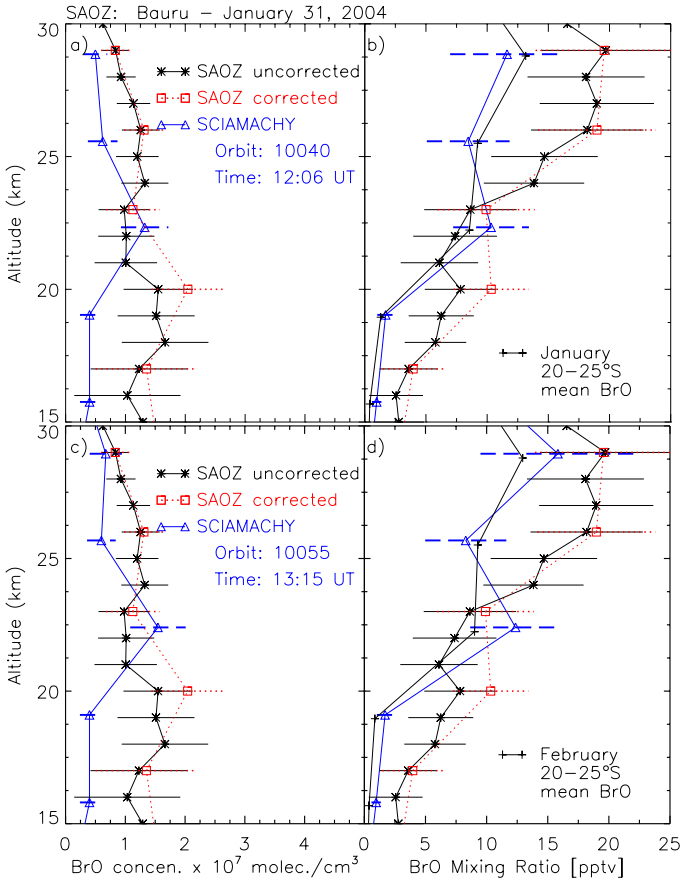

Fig. 7. Same as Fig. 6 but for a comparison with the SAOZ balloon flight on 31 January 2004 from Bauru (22.4° S, balloon SZA=80.2° (p.m.)).

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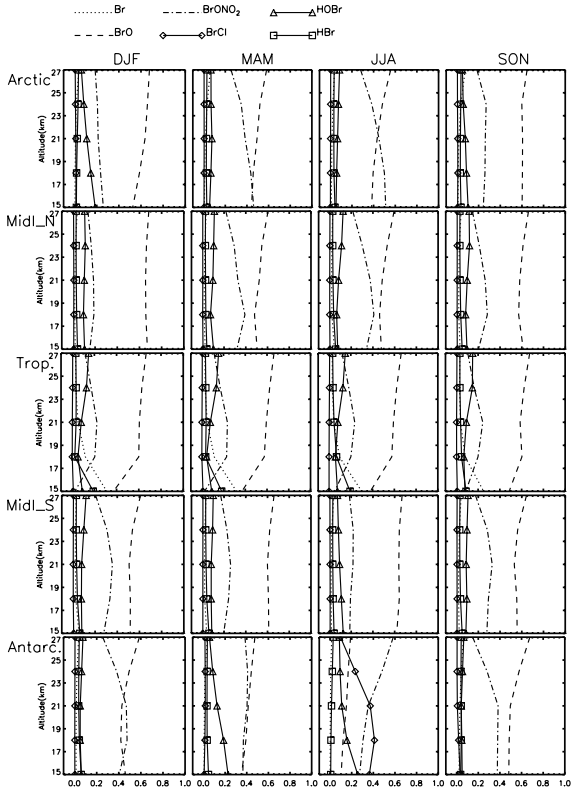

Fig. 8. Partitioning of bromine species as calculated by the 1-D photochemical model. The model was constrained by SCIAMACHY NO_2 measurements. Calculations were performed for the four seasons December/January/February (DJF), March/April/May (MAM), June/July/August (JJA) and September/October/November (SON) and five latitude bands: Arctic (north of 60° N), northern hemisphere mid-latitudes (30° N–60° N), tropics (30° S–30° N), southern hemisphere mid-latitudes (30° S–60° S), and Antarctic (south of 60° S).

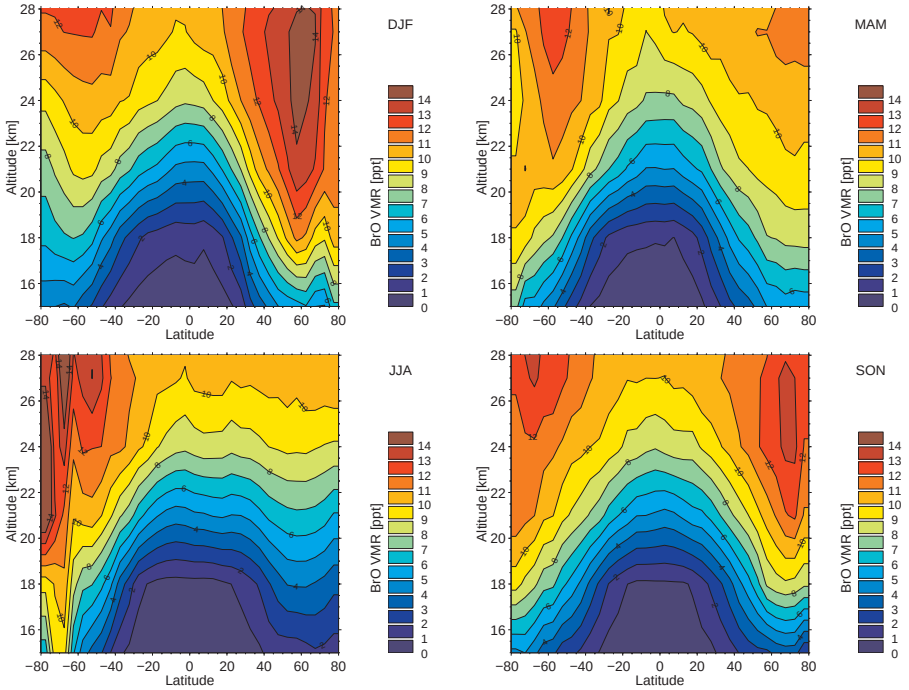

Fig. 9. BrO climatology derived from SCIAMACHY observations during 2003 and 2004. Data have been averaged for the four seasons December/January/February (DJF), March/April/May (MAM) June/July/August (JJA) and September/October/November (SON).

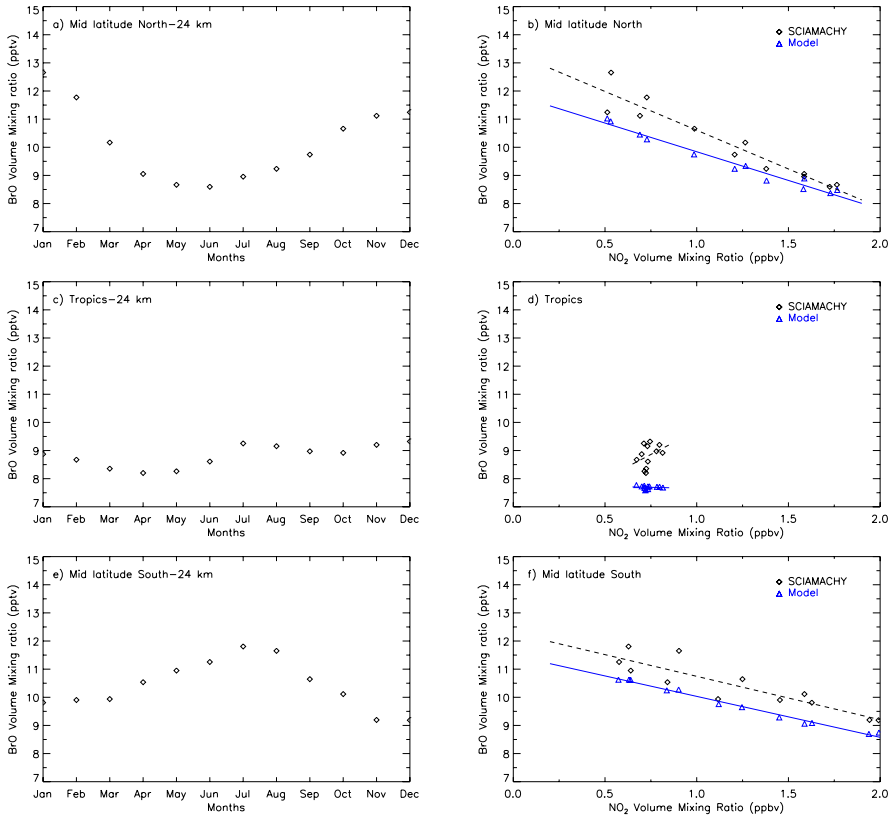

Fig. 10. Seasonal variation of BrO and its relation to NO_2. Panels **(a)**, **(c)**, and **(e)** show the seasonal variation of BrO at 24 km for northern hemisphere mid-latitudes, tropics, and southern hemisphere mid-altitudes, respectively. Panels **(b)**, **(d)** and **(f)** show the corresponding relation of BrO to the observed NO_2 mixing ratios. The red points are the data of November and December 2004 which are not used in correlation. For comparison also the relation between NO_2 and BrO from the photochemical model is shown.

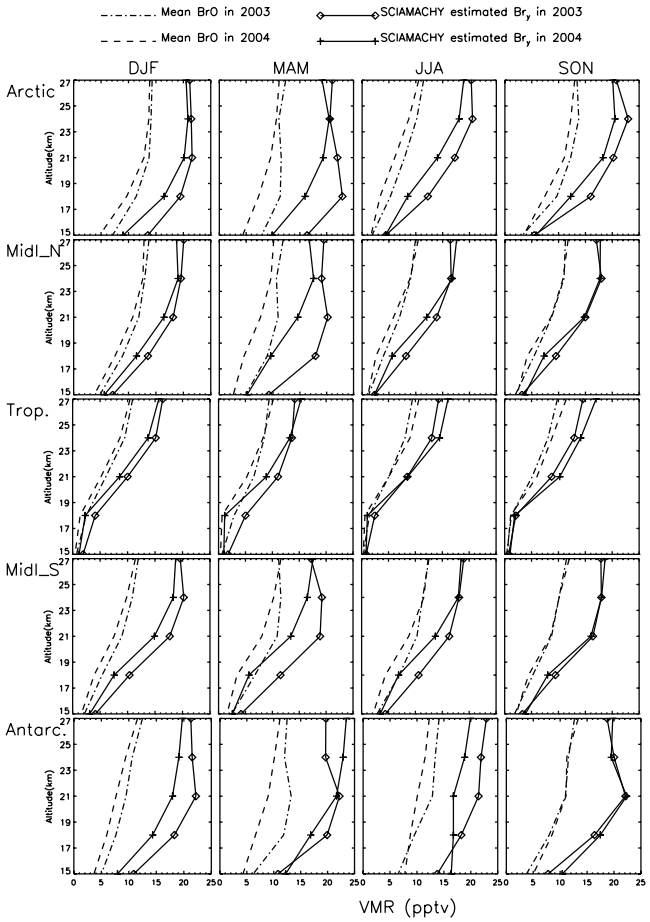

Fig. 11. Seasonal, zonal mean BrO VMRs for the two years 2003 and 2004 along with estimated Br_y for the same period.